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Morpholine–β-iodophenylacetylene (1/1) revisited: an exceptionally short I···N contact

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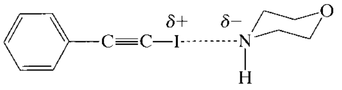
The title complex, $C_8H_5I\cdot C_4H_9NO$, has an intermolecular charge-transfer bond N···I of 2.712 (2) Å, shorter than supposed earlier and the shortest known so far. Morpholine molecules related by a b translation are linked to form a chain by N—H···O hydrogen bonds [N···O 3.110 (3) Å].

Comment

Morpholine and β-iodophenylacetylene react exothermically to form a stable 1:1 complex, first prepared by Southwick & Kirchner (1962), who suggested the charge-transfer structure, (I), on the strength of spectroscopic evidence. A single-crystal X-ray diffraction study (Baughman, 1964) confirmed structure (I), with a rather short intermolecular N···I contact of *ca* 2.9 Å. However, the accuracy of the structure, determined by Fourier projections, was not high (R = 0.18).



(I)

The present study generally confirmed the earlier one, but is of much higher accuracy and at low temperature. Morpholine molecules related by a b translation, are linked into a chain by N4—H4···O1 hydrogen bonds [N···O 3.110 (3), N—H 0.93, H···O 2.19 Å, N—H···O 173°]. The heterocycle adopts a chair conformation, with the total puckering amplitude (Cremer & Pople, 1975) Q_T = 0.550 (3) Å. The I—C18 bond points directly at the lone electron pair of the N4 atom. The C11—C17≡C18—I···N4 chain is practically linear: the maximum displacement from the best weighted least-squares line through it involves N4 which is 0.207 (4) Å from the line. The angle between this chain and the phenyl plane is 1.9 (2)°. The mean planes of the phenyl and morpholine groups form a dihedral angle of 49.9 (5)°. The I···N4 distance [2.712 (2) Å] proved much shorter than that reported by Baughman (2.9 Å), and is by far the closest intermolecular I···N contact known (with an I atom covalently bonded to carbon rather than halogen). The shortest such I···N contacts reported before, 2.93–2.95 Å, involved cyano-group nitrogen (Borgen *et al.*, 1962; Imakubo *et al.*, 1995), and the shortest one involving sp^3 nitrogen was 2.99 (3) Å in the urotropine–iodoform complex (Dahl & Hassel, 1970).

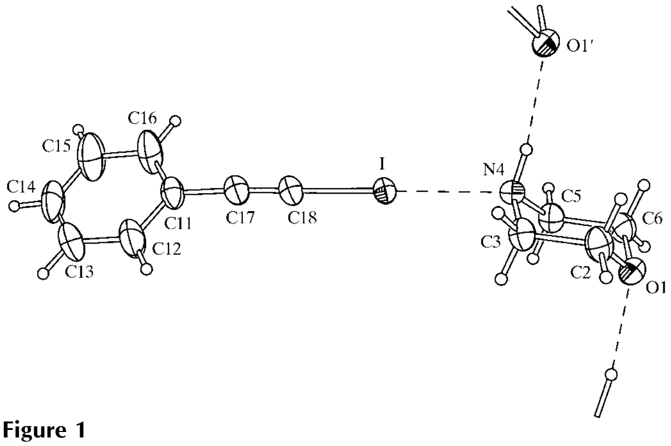


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids, and the hydrogen bonds and charge-transfer interactions.

The sum of van der Waals radii of I and N is variously estimated as 3.53 (Bondi, 1964), 3.64 (Zefirov & Zorkii, 1989) and 3.67 Å (Rowland & Taylor, 1996) in an isotropic model. The 'shape' of the I atom is in fact anisotropic, with the smallest size along the continuation of the C—I bond, where an I···N van der Waals contact of 3.36 Å can be expected (Nyburg & Faerman, 1985). By any reckoning, the distance in (I) reveals a strong charge-transfer interaction, probably enhanced by high electronegativity of the ethyne group, estimated as 3.1 in Pauling's scale (Batsanov, 1990), *i.e.* exceeding that of Cl (3.0).

Experimental

The title complex was prepared according to the method of Southwick & Kirchner (1962).

Crystal data

$C_8H_5I\cdot C_4H_9NO$
M_r = 315.14
Monoclinic, $P2_1/c$
a = 8.867 (1) Å
b = 4.8579 (2) Å
c = 29.390 (2) Å
β = 96.05 (1)°
V = 1258.9 (2) Å^3
Z = 4
D_x = 1.663 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 470 reflections
θ = 12–23°
μ = 2.519 mm^{-1}
T = 150 (2) K
Plate, colourless
0.32 × 0.30 × 0.12 mm

Data collection

Siemens SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: by integration (*XPREP* in *SHELXTL*; Sheldrick, 1995), before correction $R_{\rm int}$ = 0.080
$T_{\rm min}$ = 0.520, $T_{\rm max}$ = 0.752
10 880 measured reflections
3316 independent reflections
3136 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.027
$\theta_{\rm max}$ = 29°
$h = -12 \rightarrow 12$
$k = -6 \rightarrow 6$
$l = -39 \rightarrow 30$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.058$
$S = 1.295$
3316 reflections
136 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0062P)^2 + 1.8187P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.83$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I—C18	2.053 (3)	C3—N4	1.473 (4)
I—N4	2.712 (2)	N4—C5	1.471 (4)
O1—C6	1.429 (4)	C5—C6	1.517 (4)
O1—C2	1.430 (4)	C11—C17	1.438 (4)
C2—C3	1.518 (4)	C17—C18	1.201 (4)
C18—I—N4	177.84 (10)	C5—N4—C3	110.0 (2)
C6—O1—C2	110.8 (2)	C5—N4—I	112.09 (17)
O1—C2—C3	110.5 (2)	C3—N4—I	108.20 (16)
N4—C3—C2	112.1 (2)	C17—C18—I	176.5 (3)

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1436). Services for accessing these data are described at the back of the journal.

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